Comparison of Two Receptor Model Techniques for the Size Fractionated Particulate Matter Source Apportionment

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ABSTRACT

The goal of the study is to investigate elemental concentrations and source signatures of particulate matter at a selected receptor site in an urban area Navi Mumbai which is one of the hot spots of India with heavy industrialization. To achieve the objective, particulate matter samples were collected from 2008–2010 using Gent sampler with the automatic dichotomous size segregation unit. It was observed that the three year average concentrations of coarse ((PM$_{10-2.5\mu m}$) and fine (PM$_{2.5\mu m}$) fractions of PM were 89.92 (µg m^{-3}) and 42.25 (µg m^{-3}) respectively which were higher than the national standards prescribed by Central Pollution Control Board (CPCB), India. Subsequent elemental analysis of air filters using INAA and EDXRF showed marginally higher levels of anthropogenic derived elements. Furthermore, in the present study potentially contributing sources of coarse and fine PM were identified using two different receptor model techniques Factor Analysis (FA) and Positive Matrix Factorization (PMF). Six possible contributing sources of coarse fraction and seven probable sources of fine PM were identified by both the techniques. Further, sources identified by the receptor techniques and the comparability between the two techniques were also evaluated.

Keywords: Coarse; Fine; Receptor model; FA-MLR; PMF.

INTRODUCTION

Particulate pollution has been an area of major scientific interest over the past decade considering its adverse effects on human health and welfare. The increased concern for Particulate Matter (PM) is primarily related to their recognized adverse effects on public health, sensitive ecosystems and climate. Recent research and epidemiological studies strongly support that the elevated levels of fine particulate matter (PM$_{2.5\mu m}$, PM of size ≤ 2.5 µm) concentrations were associated with more fatalities when compared to coarse particulate matter (PM$_{10-2.5\mu m}$, PM of size 10–2.5 µm) (Dai *et al.*, 2014). Although there is no evidence to pinpoint any single feature or component of PM as the cause for the observed epidemiological effects, it is apparent that metals contribute to the toxic and carcinogenic effects associated with exposure to airborne PM and particularly for this reason monitoring as well as assessment of PM has emerged as the object of several epidemiological studies (Kawata *et al.*, 2007). In addition, trace metals are proven to be useful tracers and are extensively used to identify sources of emissions to be targeted by the emission reduction policies.

Therefore, monitoring of elemental composition of PM has become a crucial part of air quality programs in many countries around the world. Also, from a mechanistic perspective, it is highly plausible that the chemical composition of particulate matter would better predict health effects than other characteristics, such as PM mass or size. This is consistent with the large number of laboratory studies that have demonstrated compositional variability in PM toxicity and epidemiologic studies that portray the regional heterogeneity in PM-related health effects.

Particulate matter is a critical pollutant for most of the cities worldwide and particularly for the Asian cities. Megacities of India are no exception to the global pattern of deteriorating urban air quality. Indian cities are among the most polluted in the world, with concentrations of a number of air pollutants being well above the recommended World Health Organization (WHO) levels and Indian national air quality limits. The Central Pollution Control Board (CPCB) of India, under the Ministry of Environment and Forests, has stipulated national ambient air quality standards for twelve key pollutants including particulate matter below 2.5 µm and 10 µm (NAAQS, 2009). The CPCB prescribed annual and 24 hours average standards for PM$_{10}$ is 60 µg m^{-3} and 100 µg m^{-3} respectively. Air pollution in India has been aggravated over the years and is restricted mostly to urban areas, where automobiles are the major contributors, and to a few other areas industries and thermal power plants (Dubey and Pervez, 2008). Therefore in general, the

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major sources of air pollution in the country are identified as industries (toxic gases), thermal power plants (fly ash and sulphur dioxide), and motor vehicles (carbon monoxide, particulate matter, hydrocarbons and oxides of nitrogen). Major polluting industries and automobiles emit tonnes of pollutants every day, putting citizens, at great health risk. This has led to a high incidence of associated health effects on the population manifested in the form of sub-clinical effects, use of medication, reduced physical performance, frequent medical consultations and hospital admissions with complicated morbidity and even death in the exposed population. Respiratory infections account for 10.9 per cent of the total burden of diseases in India, which may be due to both the presence of communicable diseases and high air pollution levels (World Bank, 1993).

The need of knowledge on occurrence, source strengths, distribution and fate of atmospheric pollutants is increasing. This knowledge becomes crucial in the effective reduction of atmospheric levels of chemical substances like trace elements in microenvironments that are harmful for human health and the environment. The only mechanism that ultimately leads to the cost effective reduction in population exposure is identification of sources that release various toxic substances into atmospheric air. Knowing the sources also allows prioritization of substances/sources that are contributing significantly to the target population exposure. Also identifying major contributing sources elevating ambient concentrations of critical pollutants is the first step toward designing an effective policy package for air quality management. Therefore, the essentiality of source identification introduced various mathematical multivariate techniques and the different existing source apportionment techniques are mainly based on source markers, chemical mass balances, and statistical regression and factor analyses. Chemical Mass Balance (CMB), Factor Analysis (FA) and Positive Matrix Factorization (PMF) are the most effectively and commonly used receptor model techniques for the identification and apportionment of potential sources of atmospheric particulate matter. While each of these methods varies in their approach to grouping PM components and as mentioned above all are based on the principle of mass balance, in which a chemically speciated sample (or series of samples) is assumed to be composed of a linear combination of contributions from a limited number of unique factors.

The scope of the present study is based on an integrated approach which includes (i) Monitoring and characterization of size fractionated particulate matter (ii) Source identification and apportionment using two receptor techniques such as FA and PMF as well as validation of the identified sources. The study is also focused keenly in the comparison of source apportionment results obtained after the application of two most widespread receptor models (FA and PMF). Attempt is also made to determine the percentage contribution of various sources and to validate the results derived from the models using four distinguished steps by analyzing model performance, source identification, source profiles and source contribution.

MATERIALS AND METHODS

Sampling

Sampling of coarse and fine fractions of PM was carried out during 2008–2010 at Vashi, Navi Mumbai. The Thane Belapur Industrial Area (TBIA) of Navi Mumbai is considered as the industrial capital of Maharashtra state and also one of the biggest industrial sectors of Asia. It is situated along the Thane creek and 40 percent of its total area is occupied by more than 1,200 industrial units comprising chemical, bulk drugs and intermediates, dye and dye intermediates, pharmaceutical, pesticide, petrochemical, engineering good and textile manufacturing industries. The sampling was performed at a residential place nearby TBIA to study the impact of industrial emissions on a residential area.

A size segregation automatic dichotomous Gent sampler was used to collect two ranges of air particulate samples. It has an inlet with a PM_{10} cut-off, which collects only particles smaller than 10 μm. The particles are then size-segregated into fine particles smaller than 2.5 μm and coarse particles between 2.5 and 10 μm ($PM_{2.5-10}$). The particles were collected on nuclepore polycarbonate membrane filters with 8 and 0.4 μm pore size for coarse and fine particulate matter, respectively. The average sampling flow rate used was 16 L min^{-1}. 24 h representative samples were collected at the sampling site twice a week and about 275 samples were collected during the study period. A ^{210}Po charge eliminator was used to neutralize the charge accumulated on the surface of the filters before weighing. All the collected samples were then weighed using a Mettler balance with readability of 10 μg.

Elemental and BC Characterization

Air filter samples were analysed using multielemental methods such as EDXRF and INAA techniques. Characterization for 16 elements were carried out using an EDXRF spectrometer of Xenemetrix (Model Ex-6600) provided with the liquid nitrogen cooled Si(Li) detector of 20 mm^2. The resolution of the detector was 150 eV at 5.9 keV Mn $K_α$ X-rays. The system is equipped with a oil cooled Rh anode X-ray tube as the primary excitation source with the maximum operating voltage and current as 60kV and 6.6 mA respectively. The concentrations of 16 elements such as Na, Mg, Al, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Pb and Br were measured following a three step procedure where suitable secondary targets were used in each step and the operating parameters such as current, voltage and time of counting were optimized (Supp. 1). Suitable thin film standards from micro matter was used for the calibration of EDXRF system and (National Institute of Standards and Technology) NIST–SRM 2783 was used for the quality control.

Trace elements such as Sc, Co, As, Se and Sb were measured using INAA. For trace element analysis using INAA, filter samples were co-irradiated with the standard for 7 h continuously in the reactor at a flux of $1 × 10^{12}$ n cm^{-2} sec^{-1}. For the purpose of quality control NIST–SRM 1648 was used. The irradiated samples are then analysed by

gamma spectrometry using a High Purity Germanium coaxial P-type detector with 50% relative efficiency and with an energy resolution of 2 keV at 1,332 keV energy. Information regarding elemental analysis using INAA is presented elsewhere in detail (Kothai *et al.*, 2011).

Black Carbon (BC) concentrations were measured only in the fine fraction filters, prior to elemental analysis. BC in fine filters were determined by reflectance method using EEL Smoke stain reflectometer (Model 43D). Reflectometer has been calibrated using preselected clean control filter taken from the same batch and the calibration was repeated after the analysis of few filter samples as mentioned by Vallius *et al.* (2005).

Source Apportionment Techniques

The fundamental principle of receptor modeling is that mass conservation can be assumed and a mass balance analysis can be used to identify and apportion sources of airborne PM in the atmosphere. The approach to obtaining a data set for receptor modeling is to determine a large number of chemical constituents such as elemental concentrations in a number of samples. A mass balance equation can be written to account for all j chemical species in the i samples as contributions from p independent sources,

$$X_{ij} = \sum_{p=1}^{p} g_{ip} f_{jp} + e_{ij} \qquad (1)$$

where, x_{ij} is the measured concentration of the jth species in the ith sample, f_{jp} is the concentration of the jth species in material emitted by source p, g_{ip} is the contribution of the pth source to the ith sample, and e_{ij} is the portion of the measurement that cannot be fit by the model. Therefore Eq. (1) assumes that the measured parameters or concentrations x_{ij}, (apart from noise) are a weighed (scores, g_{ip}) sum of a reduced number (N << I or J number of samples or number of variables) of contributions from distinct environmental sources. Written in matrix form the same bilinear equation is represented as Eq. (2),

$$X = GF^{T} + E \qquad (2)$$

where, now X is the matrix of all measurements (j = 1, ..., J variables in i = 1, ..., I samples) G is the matrix of score profiles (distribution of the P contamination sources among samples), F^{T} is the matrix of loading profiles (composition of the P composition sources) and E is the noise or error matrix containing the variance not explained by the model defined by the P environmental sources described in G and F. Since only X is known initially, the matrix decomposition described by Eqs. (1) and (2) is ambiguous (not unique) unless constraints are applied. The number of existing source apportionment techniques based on this approach is relatively large. In this study two widely applied techniques like Factor Analysis (FA) and Postive Matrix Factorization (PMF) were employed for source identification and apportionment. The mathematical details of FA along with Multiple Linear Regression method is explained elsewhere in detail (Kothai *et al.*, 2008). Principal Component Analaysis (PCA), a most common form of FA is used in this study to solve the factor analysis problem in FA-MLR studies.

In the case of PMF technique, it solves the general receptor modeling equation using a constrained, weighted, least squares approach. These methods place restrictions on the possible source profiles defined in G and F^{T}, to require them to met certain physical constraints (e.g., non-negative source impacts and composition) instead of purely based mathematical constraints like orthogonality or variance independency. Generally, FA based methods are essentially based on eigenvector analysis, which in fact can be also considered as a least-squares analysis using a particular set of constraints and minimizing the sum of squared residuals for the model described by Eqs. (1) and (2), Positive Matrix Factorization (Paatero, 1997) takes a very different approach to the same factor analysis problem.

The PMF 3.0 model requires two input files: one for the measured concentration of the species and one for the estimated uncertainty of the concentration. In the concentration file, missing values (denoted by the value of –999) were replaced by the median value of the species and assigned an uncertainty value of 4 × standard deviation (sd) by this model. The uncertainty of the concentration was estimated as:

For concentrations < DL: Uncertainty = 5 × DL/6 (3)

For concentrations ≥ DL: Uncertainty (4)
= (DL^{2} + Precision^{2})$^{0.5}$

Concentrations beyond 4 × sd from the average concentration of the species were assigned a large uncertainty value of 10 × sd to minimise the distortion of data set by these outliers. Categorisation of quality of data was based on the signal to noise ratio (S/N) and the percentage of samples above DL. To reduce the weight in the solution, species that have a signal to noise (S/N) ratio between 0.2 and 2 and those that have MDL values more than 50% were considered as weak variables. The model was ran in the default robust mode to decrease the influence of extreme values on the PMF solution, and the FPEAK parameter was applied to control rotational ambiguity. Uncertainties in the source profiles were estimated by bootstrap procedure, provided by the EPA PMF software. The estimated uncertainty by the bootstrap analysis accounts for several sources of error, including temporal variation of PM source profiles, measurement errors, and errors in the modeling process, such as rotational ambiguity and mis-specified number of factors (Hasheminassab *et al.*, 2014).

RESULTS AND DISCUSSION

Concentrations of Particulte Matter and Trace Metals

The overall three year average concentration of PM$_{2.5–10}$ and PM$_{2.5}$ were 89.92 (μg m^{-3}) and 42.25 (μg m^{-3}) and the highest concentration was observed to be 296.45 (μg m^{-3}) and 93.33 (μg m^{-3}) respectively. The PM$_{10}$ levels of the study site are found to be within the average ranges of the data collected across India (CPCB, 2012). But the annual

average of PM_{10} is observed to be 132.17 µg m^{-3} and is more than two times above the standard set by National Ambient Air Qualtiy (60 µg m^{-3}) for PM_{10}. As regards fine particulate matter, the annual average $PM_{2.5}$ concentration was marginally higher than the NAAQ standard prescribed by CPCB. The annual average values of each sampling year depicted a slightly decreasing trend in both the fractions. Particularly, in the coarse fraction remarkable decrease is observed from 2008 to 2009. The decrease in concentration cannot be attributed to any specific reason, since the mean particulate matter concentration has been fluctuating throughout India over the years and no definite trend has been observed as the major contributing sources of PM in this fraction are natural dust, resuspension of dust etc. The seasonal analysis of the data displayed highest concentration during winter and lowest during the monsoon season in both the size fractions.

Chemical characterization of PM revealed coarse fraction metals ranged from 4.74–6229.58 ng m^{-3}. The lowest concentration was measured for Selenium and the highest concentration was for Silicon. In the case of fine fraction lowest concentration measured corresponded to Scandium, whereas the highest concentration was measured for Sulphur. The average concentrations of elements in fine PM varied from 2.46–1615 ng m^{-3}. The average concentrations of the coarse and fine fractions of PM and the measured elements are presented in supplement (Supp. 2).

Further, seasonal variations of the characterized trace metals were investigated based on the seasons of the year. For this purpose, entire year was divided into four seasons: winter (December, January and February), summer (March, April and May), monsoon (June, July, August and September) and post monsoon (October and November) based on the regional meteorological conditions. Prior to the seasonal analysis trace metals were grouped into into three categories based on their similar variations and behavior. First group consist elements like Fe, Sc, Ti, Al, Ca, Mg, Na, K Br and Cl, which are expected to be of natural origin. Among these elements crustal and marine based elements are included. These elements showed a pattern with a maximum during the summer season and a minimum during monsoon implying maximum reentrainment of soil dust due to drought as well as increased evaporation of marine sea salt during the summer season. Second group of elements with V, Ni, S, As and Se showed distinctly higher values during winter. Especially, all the five elements are apparently originated from anthropogenic emissions and interestingly strength of these elements found to be stronger mainly in the fine fraction which can be attributed to both atmospheric stability conditions and additional emissions sources during winter (Van Zyl *et al.*, 2013). Seasonal behavior of third group of elements(Cr, Co,Cu, Pb, Sb, Zn and P) showed contributions from both natural and anthropogenic sources. The concentration levels indicated input from natural sources mainly in the coarse fraction and anthropogenic source contribution in the fine fraction. Also in these cases the seasonal behavior becomes more complex as the fine fraction increases during winter while the coarse fraction increases during summer (Canepari *et al.*, 2013).

Source Identification of Coarse PM Using FA

The potentially contributing sources of coarse and fine particulate mass in the study area were first identified using principal component analysis technique followed by varimax rotation. The identified sources of coarse PM using FA technique are given in Table 1.

Six probable sources explaining 93.86% of the total variance were identified for coarse PM. Among the sources extracted for the coarse fraction crustal source with Mg, Al, Si, Ca, Ti, Fe and Sc as main tracers was identified as the major contributing source. Around 26.6% of the total variance was explained by the soil derived source in the coarse fraction. Factor 2 was identified as fugitive dust comprising Mn, Co, Zn, Pb and Sb. This factor appeared to represent diffuse pollution sources from automobile emissions, road dust and mechanical abrasion blown by traffic and wind (Kar *et al.*, 2010).

Third factor with P, S, As and Se explaining 14.9% of the variance can be labeled as coal combustion source, considering As and Se as the prominent markers of coal combustion. Factor 4 was clearly industrial because it is correlated with elements such as V, Cr, Ni and Cu, as these elements are generally of industrial origin. However, the elements grouped in the fourth factor suggests that the tracer elements of oil combustion (V and Ni) found to be merged along with the industrial source emitting Cu and Cr which could not be resolved as a separate factor. Factor 5 in coarse fraction was associated primarily with sea salt emission, because characteristic elements for this source Na, Cl, K and Br as discussed by (Zhang *et al.*, 2010) were observed to have very high loadings and this factor explained 13.6% variance. The elements like Mg, Al, Si, S and Ca had a higher loading on the final source or factor 6. The marker elements associated with this factor represent the emissions from activities related to cement or construction work. Specifically, high loading of Ca (Hu *et al.*, 2013). The loading of the elements were comparatively lower than the other factors but surprisingly this source could be resolved from the crustal source pinpointing the substantial contribution from construction activities. Since the fingerprint elements in this factor were observed to be similar as that of soil factor, this has been verified by analyzing the elemental ratios. Where, except Ca/Al ratio, Si/Al, Fe/Al, Ti/Al and Mn/Al ratios varied insignificantly. Very high ratio of Ca/Al (3.8) was observed in the sixth source profile in comparison with soil and fugitive dust sources which comprised the Ca/Al ratio around 1.2. Following the ratio analysis the last factor was attributed as emissions from construction work. Also, The MPCB report on industrial activities in Navi Mumbai insists that besides the industrial activities in MIDC area, falling sources like quarries, stone crushers and contruction activities taking place in huge quantum and also impacts on air quality in Navi Mumbai region (MPCB, 2010). It should be pointed out that the six factors resolved in the coarse particulate matter satisfactorily explained 93.8% of the total variance and consequently, the addition of more factors was not indicated.

Source Identification of Fine PM Using FA

Factor analysis of fine particulate matter resolved seven

Table 1. Factor Analysis (FA) with varimax rotation for all $PM_{2.5-10}$ data from vashi site (n = 275).

Elements	Soil	Fugitive dust	Coal combustion	Industry	Sea salt	Construction	Communality
Na	0.226	0.216	0.013	0.021	**0.911**	0.151	0.951
Mg	**0.811**	0.047	0.017	0.042	0.11	**0.562**	0.990
Al	**0.851**	0.064	0.001	–0.001	0.002	**0.504**	0.982
Si	**0.825**	0.069	–0.001	–0.003	0.061	**0.511**	0.950
P	–0.023	0.107	**0.912**	0.181	0.008	–0.062	0.880
S	0.005	0.011	**0.861**	0.014	0.009	**0.506**	0.998
Cl	–0.072	0.124	0.051	–0.024	**0.941**	0.127	0.925
K	**0.537**	0.024	0.012	0.002	**0.836**	0.006	0.988
Ca	**0.711**	0.004	0.002	–0.001	0.016	**0.702**	0.999
Ti	**0.942**	0.079	0.024	0.009	0.008	0.221	0.943
V	0.057	0.114	0.236	**0.932**	0.007	–0.016	0.941
Cr	0.263	0.286	0.218	**0.884**	0.013	0.021	0.981
Mn	**0.801**	**0.586**	0.007	0.006	0.004	0.014	0.985
Fe	**0.938**	0.214	0.059	0.086	0.021	0.224	0.987
Co	0.223	**0.903**	0.093	0.068	0.006	0.092	0.887
Ni	0.021	0.026	0.186	**0.941**	0.005	0.008	0.921
Cu	0.215	0.178	0.147	**0.896**	0.084	0.075	0.915
Zn	0.083	**0.912**	0.168	0.126	0.091	0.035	0.892
Br	0.095	0.047	0.071	0.112	**0.914**	0.091	0.872
Pb	0.097	**0.887**	0.281	0.152	0.002	–0.021	0.899
Sc	**0.916**	0.312	0.046	–0.053	0.006	0.092	0.950
As	0.095	0.175	**0.922**	0.091	0.009	0.011	0.898
Se	0.068	0.172	**0.914**	0.096	0.018	0.085	0.886
Sb	0.143	**0.914**	0.205	0.076	0.019	0.025	0.905
Eigen value	6.389	4.037	3.590	3.464	3.282	1.763	
% Variance	26.622	16.821	14.960	14.433	13.678	7.346	93.86

independent sources explaining a total variance of 93.7%. The factor loadings obtained were presented in Table 2.

Results show factor 1 with high loadings of Mg, Al, Si, Ca, Ti, Fe and Sc and accounted for a variance of 24.4%. This factor with the strong loadings of crustal elements confirms the soil contribution to the particulate matter. Factor 2 had high loadings on Si, Mn, Co, Zn and Pb and accounted for another 15.1% of the total variance. As mentioned in the coarse fraction, this factor could be identified as fugitive dust. High loading of Si in this factor confirms the contributions from road dust. Also Zn is considered as one of the indicator of tyre wear and hence this factor could be attributed as road dust. Factor three has high loadings with P, S, V, Ni and Zn, and explained 14.4% of the total variance. Since the loadings of V and Ni were higher, this particular factor might represent industrial emissions related to oil combustion (Thurston *et al.*, 1994). Factor 4 had loading on sea salt elements, such as Na, Cl, K and Br and explained 13.8% of the variance. Factor 5 showed high loadings on As, Se and Sb and accounted for 12.3% of the total variance. This factor might represent the coal combustion processes providing possible indicator elements. Studies conducted at various coal-fired power plants and utility coal combustion proved them as one of the largest source of Se for the atmospheric particles and hence Se has been widely used as a tracer for coal burning (Ogulei *et al.*, 2005). Factor 6 had strong factor loadings on Cr and Cu, and explained another 7% of the total variance.

This factor could be attributed to the textile related industries. Since Cu and Cr complexes are mostly used in abundance in the industries of textile, dyes and intermediates, it is suspected that this could be the source of emission for these elements having high loadings in the fifth factor of fine particulates (Kothai *et al.*, 2011). Also about 6% of the industries in the nearby industrial belt comprise dye and textile industries (Srivastava and Som, 2007). Factor 7 was dominated by S and BC and explained further 6.5% of the total variance. This factor appeared to represent vehicular emission (Kothai *et al.*, 2008). As mentioned by Brito *et al.* (2013) a significant fraction of sulphur is either emitted directly from the tailpipes or quickly oxidized to the particle phase and the study further states, sulphur as one of the most abundant trace element emitted by vehicular sources. Specially, PM emitted by diesel fueled vehicles emit soot formed during combustion, heavy hydro carbons condensed or adsorbed on the soot and sulphates (Bhandarkar, 2013). Therefore, sulphur and BC together could be considered as marker elements for vehicular sources.

Both in the coarse and fine fraction soil, sea salt and fugitive dust sources found to be the common sources and in the fine fraction industrial emissions could be resolved sharply. Similar studies conducted on source identification at various places of Mumbai region also indicated crustal matter and sea salt as the main sources contributing to particulate pollution along with other sources such as oil combustion, road dust, metal industries and coal combustion

Table 2. Factor Analysis (FA) with varimax rotation for all PM$_{2.5}$ data from vashi site (n = 275).

Elements	Soil	Fugitive dust	Oil Combustion	Sea salt	Coal combustion	Industries	Vehicles	Communality
Na	0.125	0.116	0.089	**0.941**	−0.095	0.079	−0.016	0.938
Mg	**0.928**	0.143	0.021	0.286	−0.031	0.028	0.009	0.966
Al	**0.902**	0.172	0.053	−0.003	0.164	−0.032	0.076	0.880
Si	**0.862**	**0.501**	0.015	0.002	0.016	0.004	0.011	0.995
P	0.023	0.0417	**0.915**	0.001	0.132	0.185	0.175	0.922
S	0.006	0.084	**0.503**	0.063	0.241	0.095	**0.811**	0.989
Cl	0.068	0.078	0.146	**0.921**	0.093	0.063	0.027	0.894
K	0.315	0.217	0.085	**0.864**	0.251	0.054	0.083	0.973
Ca	**0.878**	0.238	0.021	0.283	0.103	0.018	0.098	0.929
Ti	**0.917**	0.243	0.013	0.008	0.108	0.082	0.112	0.931
V	0.073	0.079	**0.914**	0.008	0.103	0.093	0.174	0.897
Cr	0.127	0.138	0.218	0.013	0.051	**0.884**	0.127	0.883
Mn	0.356	**0.896**	0.214	0.016	0.089	0.042	0.019	0.986
Fe	**0.923**	0.252	0.093	0.062	0.136	0.039	0.039	0.949
Co	0.241	**0.867**	0.028	0.004	0.212	0.062	0.198	0.899
Ni	0.026	0.083	**0.893**	0.016	0.314	0.036	0.069	0.910
Cu	0.189	0.162	0.273	0.072	0.276	**0.851**	0.131	0.959
Zn	0.092	**0.815**	**0.542**	0.042	0.064	0.048	0.083	0.982
Br	0.135	0.126	0.005	**0.893**	0.169	0.182	0.093	0.902
Pb	0.014	**0.872**	0.281	0.021	0.217	0.191	0.017	0.924
Sc	**0.892**	0.361	0.035	0.011	0.014	0.012	0.009	0.928
As	0.141	0.121	0.165	0.084	**0.931**	0.012	0.113	0.948
Se	0.021	0.124	0.134	0.019	**0.892**	0.253	0.017	0.894
Sb	0.093	0.092	0.389	0.062	**0.873**	0.184	0.083	0.975
BC	0.057	0.072	0.305	0.004	0.324	0.135	**0.873**	0.987
Eigen value	6.099	3.783	3.604	3.467	3.075	1.776	1.632	
% Variance	24.396	15.132	14.417	13.868	12.301	7.105	6.527	93.74

(Sharma and Patil, 1994; Kumar *et al.*, 2001). Similarly, soil, road dust, vehicular emissions and coal combustion were proved to be the potential contributing sources of atmospheric particulate matter load in other parts of India (Gupta *et al*., 2008; Kulshrestha *et al*., 2009; Tiwari *et al*., 2009; Khare and Baruah, 2010; Shridhar *et al*., 2010). Around 42% of the total variance was explained by the soil derived source in the coarse fraction and about 39% variance was explained in the fine fraction. This revealed the association of Fe a key signature element for soil with the other crustal elements contributed from reentrained windblown crustal source (Shah and Shaheen, 2008; Gugamsetty *et al*., 2012).

Source Apportionment Using FA-MLR

In the present study, multiple regression analysis was performed following Hosiokangas *et al.* (1999). For multiple regression study finger print elements were selected based on their high loadings in a particular factor and insignificant loadings in other factors. The linear regression equations obtained for coarse and fine PM were as follows:

$$PM_{10-2.5} = \beta_0 + \beta_1 \, Si + \beta_2 \, Na + \beta_3 \, Zn + \beta_4 \, As + \beta_5 \, V \qquad (5)$$
$$+ \beta_6 \, Ca + \varepsilon$$

$$PM_{2.5} = \beta_0 + \beta_1 \, Si + \beta_2 \, V + \beta_3 \, S + \beta_4 \, Na + \beta_5 \, Cr \qquad (6)$$
$$+ \beta_6 \, As + \beta_7 \, Zn + \varepsilon$$

where, β_0 is the intercept, β_1, β_2, β_3, β_4, β_5, β_6, β_7 are the coefficients of the markers and ε is an error term. All the regression coefficients for the markers were significant and the details of the multiple regression model are presented in supplement (Supp. 3). Source apportionment of coarse particulate matter showed a maximum contribution of 26% from sea salt as the site is nearby coastal area. The crustal source contributed 20%, while the contribution from the fugitive emission was found to be 11%. Vehicular and industrial emissions contributed 10% and 11%, respectively. Source related to construction work contributed less compared to other sources and it was 6%.

In the case of fine particulate matter, the maximum mass has been contributed by vehicular sources and was around 26%. For fine mass, 13% of the mass has been contributed from industrial sources. Apart from this, specifically, oil combustion and coal combustion based industries accounted for 12% and 10% respectively of the total PM concentrations. These findings seem reasonable as most of the small scale and large scale industries situated in TTC industrial area are using oil or coal as fuel which create huge emission. Also some units are having coal fired boilers (MPCB, 2010). Natural sources like sea salt and crustal sources contributed to 12% and 6% respectively in the fine fraction. Therefore maximum percentage contribution in the fine fraction observed to be contributed from the anthropogenic sources especially from vehicular and industrial activities. Whereas,

around 50% of the particulate matter load in the coarse fraction is due to natural sources and also another 10% contribution was contributed as a result of resuspension of road dust due to heavy traffic activities near the study area. Also 38% mass found to be devoted by anthropogenic emission and the remaining 16% mass in the coarse PM is regarded as unexplained portion of the total mass. Whereas, 15% of the mass was not explained in the fine PM source apportionment. Figures depicting the percentage contributions in both the size fractions are given in supplementary (Supp. 4).

Source Identification of Coarse PM Using PMF

The coarse and fine PM speciation data was then utilized for the source identification using Positive Matrix Factorization technique to reconfirm the probable contributing sources of the study region. Fig. 1 depicts the source profiles of the six possible sources and their associated source contributions obtained by PMF technique. The bars in the profile represent the concentration and the dots denote the percentage of the species in the factor.

The first source of coarse fraction is a typical soil source with dominant high concentrations of Mg, Al, Si, Ca, Ti and Fe. The second factor found to be the sea salt source due to higher concentrations of Na, Cl and other sea salt elements. The third factor is clearly identified as fugitive road dust due to the presence of most of the soil derived elements along with the high concentrations S and tyre wear marker element Zn. In comparison with the results of FA loadings of coarse fraction fugitive dust, PMF source profile clearly indicated the major elements present in this source and confirmed that the source is road dust. The forth factor with the presence of high sulphur implies the contribution from vehicular emission but the considerable contribution of As and Se in this factor emphasize that there may be overlapping of vehicular and coal combustion sources which could not be resolved by the model. The fifth factor is characterized by many of the anthropogenically derived toxic elements like P, S, V, Cr, Ni and Cu revealing the contributions from different industrial activities. The sixth factor is Ca rich source produced by some construction activities around the sampling site. Again in this case, the detailed elemental source profile obtained from PMF model sharply presents very high concentration of Ca in this factor which helps in the distinction of construction related sources from other fugitive sources. Whereas, the factor loadings of FA indicated strong loadings of Ca with other soil derived elements but the intensity of calcium concentration becomes unclear and leading to a troublesome footing in distinguishing the source.

Source Identification of Fine PM Using PMF

A seven factor model was chosen after the analysis of fine PM data using PMF and the source profiles are provided in Fig. 2.

The first source with the tracers of crustal elements was identified as soil. In the case of forth factor of coarse fraction vehicular and coal combustion markers found to be merged. However in the fine fraction these sources have been resolved in to two different factor (Factor 3 and 4) with their respective key identifying elements. Black carbon additionally added in the fine fraction apportionment used as the second key tracer element with sulphur to identify the vehicular emissions. Forth factor represents sea salt. Fifth factor is characterized by high concentrations of Cr and Cu. Also nominal concentrations of other metals used as pigments in the textile industries are also seen in this factor and hence this can attributed to the textile industry emission. Abundant S, As and Se presence in the sixth factor confirms the contribution from coal combustion in the fine fraction PM. The final seventh source possesses similar elements as in fugitive road dust of coarse fraction and was marked as fugitive dust.

Evaluation and Comparison of FA and PMF

One of the main aspects of the present study is that two different receptor models were applied to apportion the size fractionated PM data in order to compare results and the adequacy of models. The comparability between receptor models was evaluated as a function of four parameters following the procedure of Viana *et al.* (2008) and the parameters are: (i) Model performance: The ability of the models to reproduce the measured concentrations, (ii) Source identification: The number and nature of the sources identified, (iii) Source profiles: The similarities or dissimilarities observed between the different source profiles obtained with FA and PMF, (iv) Source contribution: The quantification of the mass contribution of the sources to the total coarse and fine PM. The results of model performance and source identification by both the receptor model techniques were presented in supplementary (Supp. 5) and the detailed discussion on the verification of the model performance is presented in the subsequent sections.

Model Performance

As a first step of evaluation of the models utilized in this study the ability of each model to reproduce the daily measured concentrations of coarse and fine PM was estimated. This part of the study demands complete characterization of the filter samples. Therefore two collocated air samplers were operated together for more than six months to facilitate water soluble inorganic ions (F^-, Cl^-, NO_2^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}) and carbon (Elemental and organic carbon) characterization. Inorganic ions were measured using Ion chromatograph system and carbon analysis was performed with a DRI 2100A system. Prior to the comparison of modeled and gravimetric mass of PM, as a first step average values of cations and anions (F^-, NO_2^-, NO_3^- and NH_4^+) which are not included as elements in the model were summed. In the second step the average Organic Carbon (OC) measured in the samples were converted to Organic Matter (OM) by multiplying OC by a factor of 1.6. Finally the average Elemental Carbon (EC) measured in both the fractions were also summed with ions, organic matter together with the modeled elemental concentrations. Finally the daily measured and the modeled concentrations (Elemental concentration from model + OM + EC) were regressed. This method
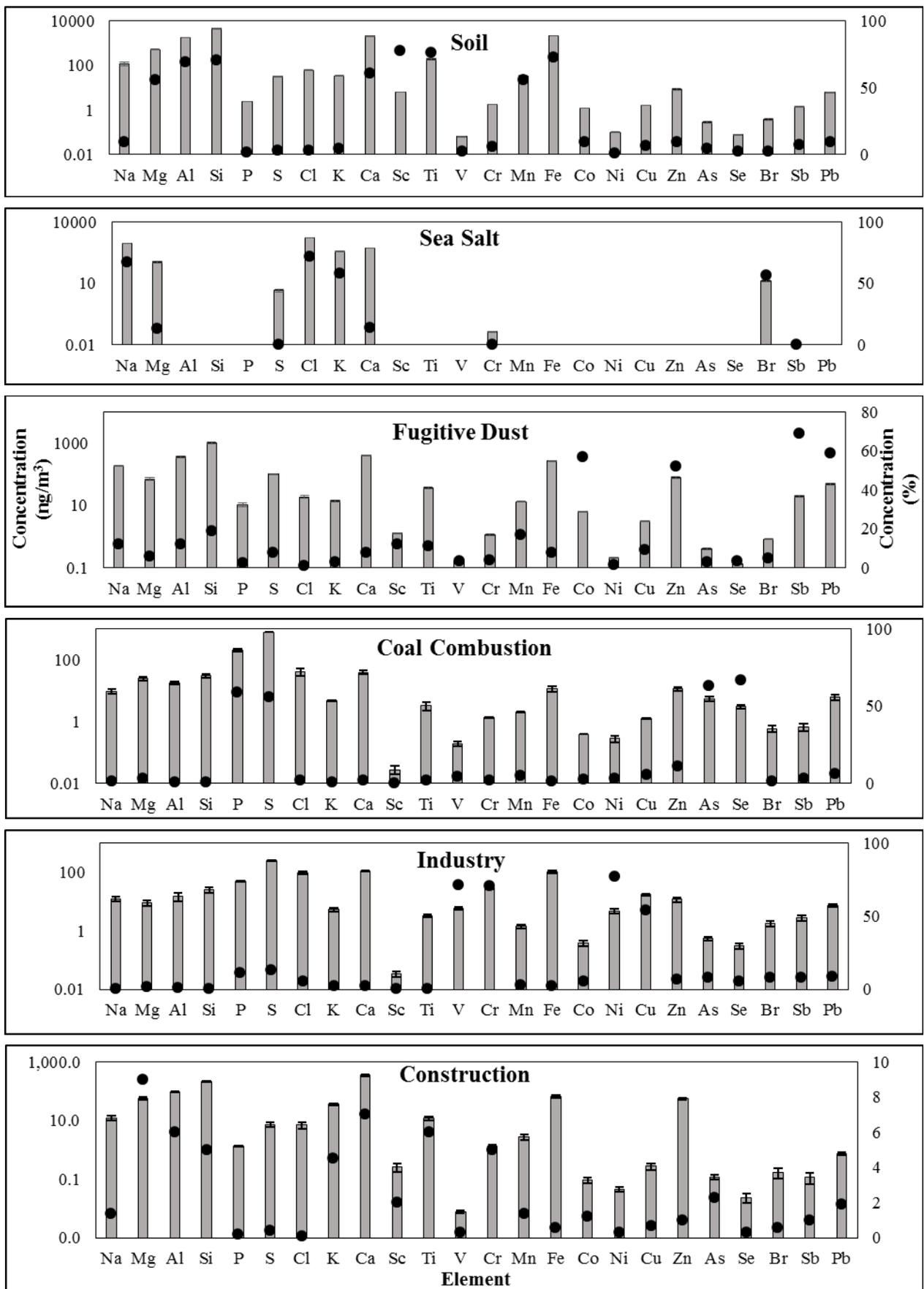
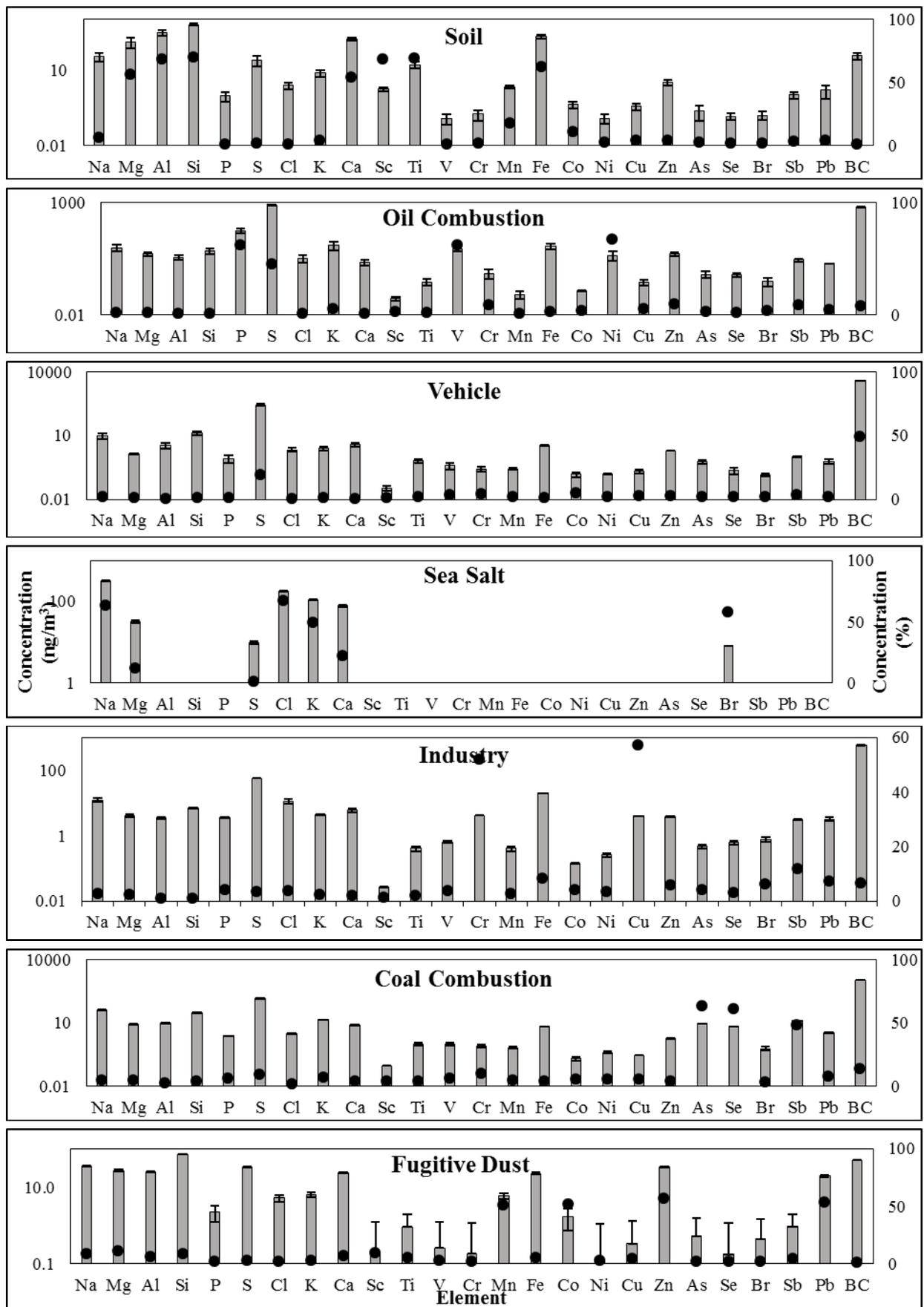**Fig. 1.** Source profiles of coarse PM resolved by PMF 3.0.

Fig. 2. Source profiles of fine PM resolved by PMF 3.0.

reproduced around 90% of the gravimetric mass in both the coarse and fine fraction PM. The average ion concentrations, OM and EC are presented in the supplement (Supp. 6). It was found that both the models provided good results regarding their ability to reproduce the measured values. The dispersion between measured and modeled data was found to be lowest for PMF (R^2 = 0.87 and 0.85 for coarse and fine PM respectively) and also the slope of the correlation curve was near to unity with the low intercept. Whereas, intercept and slope were observed to be slightly higher in the case of FA. Also, the correlation coefficient was comparably lower for FA with the R^2 = 0.83 and 0.81 for coarse and fine fraction PM. Therefore, both the models provided highly satisfactory results, but at the same time PMF showed lowest dispersion and also the average difference between modeled and measured results was found to be minimal with PMF. The regression plots of modelled and measured values are presented in supplement (Supp. 7).

Source Identification

FA and PMF models were able to distinguish 6 potentially contributing sources of coarse fraction and 7 sources for fine PM. The number of sources identified by FA and PMF were found to be similar. However, two different techniques were applied to confirm the appropriate number of sources while applying FA and PMF. In the case of FA number of factors was decided based on few aspects like, total variance explained by the resolved factors, variance explained by each factor and the eigen value of each factor. When each factor explains the maximum total variance of the data set, this set becomes completely uncorrelated with the rest of the data. The total variance explained in coarse and fine PM based on the decided number of factors were around 93.8 and 93.7% respectively. Eigen value of each identified factor in both the size fraction ranged from 7.5–1.

In the case of PMF analysis, the optimal number of factors was identified after analyzing the goodness of fit Q-values for the entire run, the scaled residual matrices, G-space plots, and physical meaningfulness of the factor profiles and contributions (Lee *et al*., 1999). The model was run for 20 times each for coarse and fine PM data set with a 6-factor and 7-factor solutions respectively. All runs converged and a global minimum was found. The Q-robust of the present study was found to be equal to the Q-true, indicating no outliers impacting the Q value. A total of 100 bootstrap runs were performed to assess the uncertainty of the factor loadings and scores. Of the 100 runs, all the 6-factors of coarse and 7-factors of fine were mapped to a base factor in every run indicating a stable result. Residuals were also found to be between 3 and –3 for all the species. Other than the model performance parameters sources were also identified and confirmed on the basis of major marker elements of the sources and the percentage of the species in each source.

A sensitivity analysis was also carried out to evaluate the performance of the receptor models regarding the identification of sources (Chow *et al*., 2007). Generally, model precision can be expressed in terms of Average Absolute Error (AAE %), which is the average of the absolute percent differences between the estimated and experimental PM data, when different number of sources or factors were considered. Number of factors varied from 3 to 8 with FA and PMF and the corresponding AAE % is presented in the supplement (Supp. 8).

For coarse particles when FA was applied, AAE improved significantly from the 3-factor to the 6-factor model. But FA produced invalid solutions for 7 and 8 factor models. Whereas, when PMF was used AAE improved progressively from 3–7 factors providing minimum AAE for 6 and 7 factor solutions. But when the F-matrix of 7-factor solution was analyzed the results had no physical meaning. When the solution was derived for 8-factor error started increasing confirming the 6-factor model selected was suitable for the coarse particulate data set. When fine PM data set was used for the source identification using FA and PMF gradual decrease in the AAE was observed from 3-8 factor solutions but abruptly higher error was attained as well as the solution was not found meaningful for 8-factor solution in both the models emphasizing that the 7-factor model is appropriate for the fine PM.

Source Profiles

Same numbers of sources have been obtained in this study for coarse and fine PM. Also it was noticed that major source fingerprints were commonly resolved by both FA-MLR and PMF source apportionment techniques as mentioned by Khan *et al*. (2012). But the source profiles obtained in both the cases cannot be compared directly. As for the FA results are concerned, the magnitude of the species contributions are in different unit because the concentration of different species were normalized prior to the analysis. But the key marker elements were clearly identified for all the sources. However, the strong loadings of a group of tracer species indicated the emission of possible source which were again confirmed by the high concentrations of those species in the respective factor profile resolved by PMF.

Source Contribution

Similar to FA-MLR, meaningful mass contributions were derived by applying multiple linear regression technique with the factor scores estimated by PMF. Since there were no straight forward method available to estimate the source contribution error or the unexplained part of metals in each source, regression analysis approach was used (Manousakas *et al*., 2015). Comparison of the two models strongly suggested that the highest contribution to the coarse fraction is from natural sources like sea salt and soil. Particularly, sea salt and construction source contribution found to be higher than FA. Percentage mass contribution from other man made sources found to vary minutely between the two models. While comparing the source contributions for fine fraction PM, vehicular emission contributed to the highest. But there was approximately 4% enhancement of vehicular contribution in FA results compared with PMF analysis. On the other hand, around 2–5% reduction was seen for coal and oil combustion based sources in FA. Contribution obtained by both the models for all the sources were comparable, especially for coarse fraction PM. However,

marginal variations of mass contributions computed by FA and PMF were observed in the case of fine fraction of the particulate matter. The details of percentage contribution by both the models are illustrated in the supplement (Supp. 9).

CONCLUSIONS

The study revealed elevated annual average concentrations of particulate matter and slightly enhanced levels of atmospheric trace metal concentrations in the study site. Identification of potential source contributors and validation of identified sources was achieved by apportioning the size fractionated atmospheric particulate matter using two multivariate receptor models such as FA and PMF. The major source categories of coarse particles were natural sources like crustal and sea salt. Whereas, emissions from vehicles and industries were found to be the dominant contributors for fine particulate matter followed by the less influential crustal and sea salt source categories. Despite the minor differences in the source profiles both the models were able to identify the main sources contributing to the PM and a reasonable agreement between FA and PMF was also observed.

SUPPLEMENTARY MATERIALS

Supplementary data associated with this article can be found in the online version at http://www.aaqr.org.

REFERENCES

Bhandarkar, S. (2013). Vehicular pollution, their effect on human health and mitigation measures. *Vehicle Eng.* 1: 33–40.

Brito, J., Rizzo, L.V., Herckes, P., Vasconcellos, P.C., Caumo, S.E.S., Fornaro, A., Ynoue, R.Y., Artaxo, P. and Andrade, M.F. (2013). Physical-chemical characterisation of the particulate matter inside two road tunnels in the São Paulo Metropolitan Area. *Atmos. Chem. Phys.* 13: 12199–12213.

Canepari, S., Astolfi, M.L., Marcovecchio, F., Maretto, M. and Perrino, C. (2013). Seasonal variation in the concentration and solubility of elements in atmospheric particulate matter: A case study at northern Italy. *E3S Web Conferences* 1: 20002.

Chow, J.C., Watson, J.G., Lowenthal, D.H., Chen, L.W.A., Zielinska, B., Mazzoleni, L.R. and Magliano, K.L. (2007). Evaluation of organic markers for chemical mass balance source apportionment at the Fresno Supersite. *Atmos. Chem. Phys.* 7: 1741–1754.

CPCB (2012). Report on National Ambient Air Quality Status and Trends in India. Central Pollution Control Board, Government of India.

Dai, L., Zanobetti, A., Koutrakis, P. and Schwartz, J.D. (2014). Associations of fine particulate matter species with mortality in the United States: a multicity time-series analysis. *Environ. Health Perspect.* 122: 837–842.

Dubey, N. and Pervez, S. (2008). Investigation of variation in ambient PM_{10} levels within an urban-industrial

environment. *Aerosol Air Qual. Res.* 8: 54–64.

Gugamsetty, B., Wei, H., Liu, C., Awasthi, A., Hsu, S., Tsai, C., Roam, G., Wu, Y. and Chen, C. (2012). Source characterization and apportionment of PM_{10}, $PM_{2.5}$ and $PM_{0.1}$ by using positive matrix factorization. *Aerosol Air Qual. Res.* 12: 476–491.

Gupta, A.K., Karar, K., Ayoob, S. and John, K. (2008). Spatio-temporal characteristics of gaseous and particulate pollutants in an urban region of Kolkata, India. *Atmos. Res.* 87: 103–115.

Hasheminassab, S., Daher, N., Ostro, B.D. and Sioutas, C. (2014). Long-term source apportionment of ambient fine particulate matter ($PM_{2.5}$) in the Los Angeles basin: A Focus on emissions reduction from vehicular sources. *Environ. Pollut.* 193: 54–64.

Hosiokangas, J., Ruuskanen, A. and Pekkanen, J. (1999). Effects of soil dust episodes and mixed fuel sources on source apportionment of PM_{10} particles in Kuopio, Finland. *Atmos. Environ.* 33: 3821–3829.

Hu, X., Ding, Z., Zhang, Y., Sun, Y., Wu, J., Chen, Y. and Lian, H. (2013). Size Distribution and Source Apportionment of Airborne Metallic Elements in Nanjing, China. *Aerosol Air Qual. Res.* 13: 1796–1806.

Kar, S., Maity, J.P., Samal, A.K. and Santra, S.C. (2010). Metallic components of traffic induced urban aerosol, their spatial variation, and source apportionment. *Environ. Monit. Assess.* 168: 561–574.

Kawata, K., Yokoo, H., Shimazaki, R. and Okabe, S. (2007). Classification of heavy metal toxicity by human DNA microarray analysis. *Environ. Sci. Technol.* 41: 3769–3774.

Khan, M.D., Hirano, K. and Masunaga, S. (2012). Assessment of the sources of suspended particulate matter aerosol using US EPA PMF 3.0. *Environ. Monit. Assess.* 184: 1063–1083.

Khare, P. and Baruah, B.P. (2010). Elemental characterization and source identification of $PM_{2.5}$ using multivariate analysis at the suburban site of north east India. *Atmos. Res.* 98: 148–162.

Kothai, P., Saradhi, I.V., Prathibha, P., Hopke, P.K., Pandit G.G. and Puranik, V.D. (2008). Source apportionment of coarse and fine particulate matter at Navi Mumbai, India. *Aerosol Air Qual. Res.* 8: 423–436.

Kothai, P., Saradhi, I.V., Pandit, G.G., Markwitz, A. and Puranik, V.D. (2011). Chemical characterization and source identification of particulate matter at an urban site of Navi Mumbai, India. *Aerosol Air Qual. Res.* 11: 560–569.

Kulshrestha, A., Satsangi, P.G., Masih, J. and Taneja, A. (2009). Metal concentration of $PM_{2.5}$ and PM_{10} particles and seasonal variations in urban rural environment of Agra, India. *Sci. Total Environ.* 407: 6196–6204.

Kumar, A.V., Patil, R.S. and Nambi, D.S.V. (2001). Source apportionment of suspended particulate matter at two traffic junctions in Mumbai, India. *Atmos. Environ.* 35: 4245–4251.

Lee, E., Chan, C.K. and Paatero, P. (1999). Application of positive matrix factorization in source apportionment of particulate pollutants in Hong Kong. *Atmos. Environ.*

33: 3201–3212.

Manousakas, M., Diapouli, E., Papaefthymiou, H., Migliori, A., Karydas, A.G., Padilla-Alvarez, R., Bogovac, M., Kaiser, R.B., Jaksic, M., Bogdanovic-Radovic, I. and Eleftheriadis, K. (2015). Source apportionment by PMF on elemental concentrations obtained by PIXE analysis of PM_{10} samples collected at the vicinity of lignite power plants and mines in Megapolis, Greece. *Nucl. Instrum. Methods Phys. Res., Sect. B* 349: 114–124.

MPCB (2010). Environmental Status and Action Plan for Prevention and Control of Pollution, Action Plan for Industrial Cluster: Navi Mumbai. Maharashtra Pollution Control Board, Government of India.

NAAQS (2009). National Ambient Air Quality Standards, CPCB.

Ogulei, D., Hopke, P.K., Zhou, L., Paatero, P., Park, S.S. and Ondov, J.M. (2005). Receptor modeling for multiple resolved species: The Baltimore supersite. *Atmos. Environ.* 39: 3751–3762.

Paatero, P. (1997). A weighted non-negative least squares algorithm for three-way 'PARAFAC' factor analysis. *Chemom. Intell. Lab. Syst.* 38: 223–242

Shah, M.H. and Shaheen, N. (2008). Annual and seasonal variations of trace metals in atmospheric suspended particulate matter in Islamabad, Pakistan. *Water Air Soil Pollut.* 190: 13–25.

Sharma, V.K. and Patil, R.S. (1994). Chemical mass balance model for source apportionment of aerosols in bombay. *Environ. Monit. Assess.* 29: 75–88.

Shridhar, V., Khillare, P.S., Agarwal, T. and Ray, S. (2010). Metallic species in ambient particulate matter at rural and urban location of Delhi. *J. Hazard. Mater.* 175: 600–607.

Srivastava, A. and Som, D. (2007). Hazardous air pollutants in industrial area of Mumbai, India. *Chemosphere* 69: 458–468.

Thurston, G.D., Ito, K. and Lall, R. (1994). A source Apportionment of U.S. fine particulate matter air pollution. *Atmos. Environ.* 45: 3924–3936.

Tiwari, S., Srivastava, A.K., Bisht, D.S., Bano, T., Singh, S., Behura, S., Srivastava, M.K., Chate, D.M. and Padmanabhamurthy, B. (2009). Black Carbon and chemical characteristics of PM_{10} and $PM_{2.5}$ at an urban site of north India. *J. Atmos. Chem.* 62: 193–209.

Vallius, M., Janssen, N.A.H., Heinrich, J., Hoek, G., Ruuskanen, J., Cyrys, Van Grieken, R., de Hartog, J.J., Kreyling, W.G. and Pekkanen, J. (2005). Sources and elemental composition of ambient $PM_{2.5}$ in three European cities. *Sci. Total Environ.* 337: 147–162.

Van Zyl, P.G., Beukas, J.P., Du Toit, G., Mabaso, D., Hendriks, J., Vakkari, V., Titta, P., Pienaar, J.J., Kulmala, M. and Laakso, L. (2013). Assessment of atmospheric trace metals in the western Bushveld Igneous Complex, South Africa. *S. Afr. J. Sci.* 110: 1–11.

Viana, M., Pandolfi, M., Minguillon, M.C., Querol, X., Alatuey, A., Monfort, E. and Celades, I. (2008). Inter-comparison of receptor models for PM source apportionment: Case study in an industrial area. *Atmos. Environ.* 42: 3820–3832.

Zhang, Z., Engling, G., Lin, C., Chou, C.C.K., Lung S.C., Chang, S., Fan, S., Chan, C. and Zhang, Y. (2010). Chemical speciation, transport and contribution of bio-mass burning smoke to ambient aerosol in Guangzhou, a megacity of China. *Atmos. Environ.* 44: 3187–3195.